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AUTHOR(S):

Osugi, Jiro; Sato, Masanori; Ifuku, Naoyuki

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THE EFFECT OF PRESSURE AND TEMPERATURE ON THE MICELLE FORMATION OF DODECYLBENZYLDIMETHYL-AMMONIUM CHLORIDE SOLUTION

BY JIRO OSUGI, MASANORI SATO AND NAOYUKI IFUKU

The electrical conductivity of the dodecylbenzyldimethylammonium chloride (DBAC) solution has been measured at high pressure up to 5,000 atm and at temperature range 25 to 45°C. The critical micelle concentration (c.m.c.) of DBAC increases at high pressure. However, it decreases gradually at higher pressures above 1,000 atm. The partial molal volume change, ΔV, for the micelle formation at one atmosphere is calculated from the thermodynamic relationship between c.m.c. and pressure. The value of ΔV decreases gradually with the increase of temperature: -2.3 cc/mole at 45°C. From the linear relationship between $-\log$ (c.m.c.) and $1/T$ at one atmosphere, it was shown that the value of the partial molal enthalpy change, ΔH, is, constant, -1.28 kcal/mole, at temperature range 25 to 45°C. By using the value of ΔV and ΔH, the partial molal entropy change, ΔS, is calculated to be about $+4.5$ cal/mole deg.

Introduction

In the previous paper[1)2)], we have reported the variation of critical micelle concentration (c.m.c.) of the aqueous solution of cationic surface active substances under high pressure at 25°C.

The c.m.c. of alkyl dodecylammonium salt solution increases with increasing pressure and above 1,000 atm it begins to decrease gradually at higher pressure. At one atmosphere, the partial molal volume change caused by micelle formation, ΔV, of alkyl dodecylammonium salt solutions is about $+3$ cc/mole regardless of the structure of their polar onium group. Besides, the pressure at which the value of c.m.c. reaches maximum is about 1,000 atm at 25°C irrespective of the structure of cationic detergents. As a results, the above mentioned phenomena have been attributed to the change of solvation of the water surrounding the micelle particles.

In order to confirm this explanation, the electrical conductivity of the dodecylbenzyldimethyl ammonium chloride (DBAC) solution has been measured at high pressure at several temperatures: 25, 35 and 45°C.

Experimentals

The commercial reagent grade substance of DBAC was used without further purification. The

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2) J. Osugi, M. Sato and N. Ifuku, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), 87, 392 (1966)

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details of the apparatus: the conductivity cell, the electrical conductivity measurement apparatus and the thermostat have been described previously[1]. The temperature of the thermostat was controlled with liquid paraffin.

Results

In Figs. 1 and 2, the change of specific conductivity of DBAC at various concentrations at high pressures up to 5,000 atm was shown at 35 and 45°C, respectively. The general features of the curves strongly resemble that measured at 25°C[1]. In the case of the sample solutions, which are below c.m.c. at atmospheric pressure, the specific conductivity is not affected remarkably by high pressures. It shows that the detergent ion behaves as a strong electrolyte at single ionic state. On the contrary, the specific conductivity of the sample solutions which are above c.m.c. at atmospheric pressure is greatly influenced by high pressures. With increasing pressure up to about 2,000 atm, the specific conductivity increases remarkably. Assuming the equilibrium between the single ions and the micellar ions

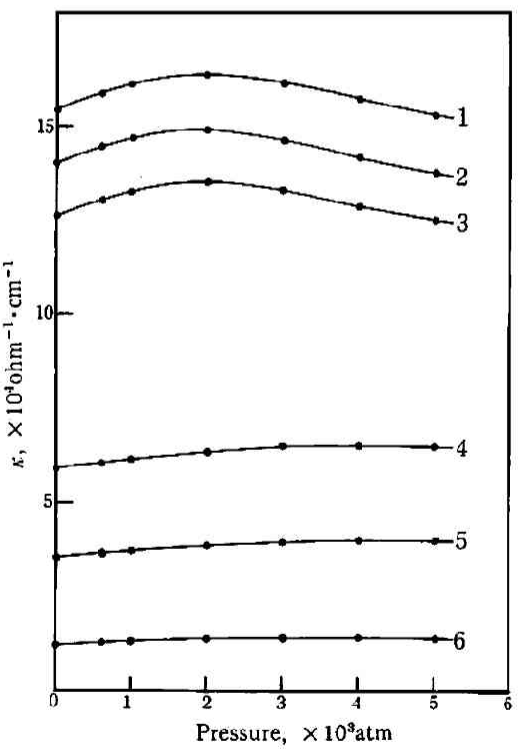

Fig. 1 Specific conductivity of DBAC at 35°C
1: 0.0215 (molal), 2: 0.0185, 3: 0.0154, 4: 0.0513, 5: 0.0031, 6: 0.0010

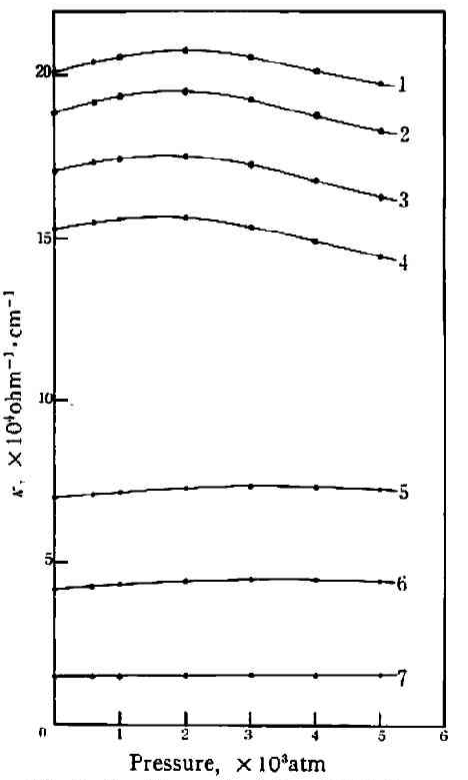

Fig. 2 Specific conductivity of DBAC at 45°C
1: 0.0236 (molal), 2: 0.0215, 3: 0.0185, 4: 0.0154, 5: 0.0051, 6: 0.0031, 7: 0.0010

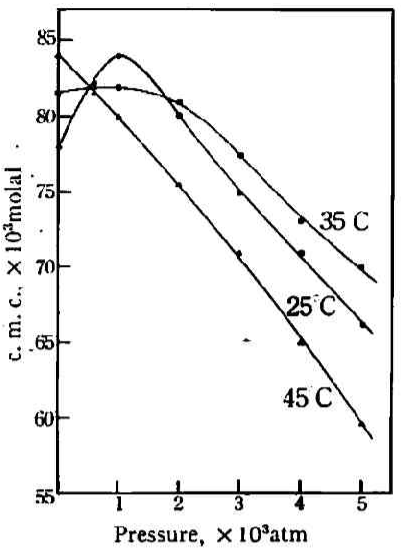

Fig. 3 Variation of c.m.c. with high pressure at various temperature

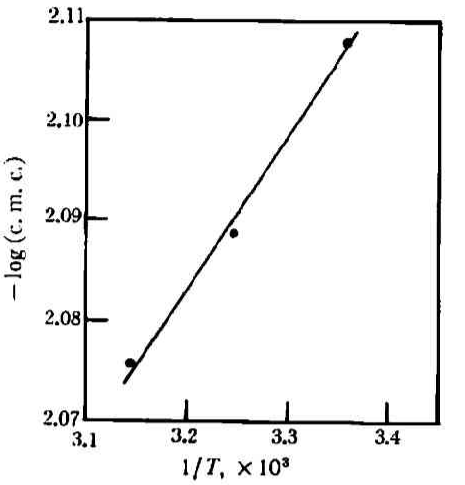

Fig. 4 Relationship between $-\log(\text{c.m.c.})$ and $1/T$

of the detergent, these phenomena could be explained partly by the dissociation of the micellar counter ion to the free single ion owing to the increase of pressure.

The values of c.m.c. at various high pressures are determined by plotting specific conductance against the concentration of DBAC. Fig. 3 shows the change of c.m.c. of DBAC with pressure at 25[1], 35 and 45°C. At 35°C the c.m.c. is not considerably affected with the increase of high pressure up to about 2,000 atm. At higher pressure, the c.m.c. decreases gradually. In this case, there is no distinct pressure at which the c.m.c. takes a maximum value as in the case of the experiment carried out at 25°C. In the experiment at 45°C, the c.m.c. decreases monotonously with the increase of pressure up to 5,000 atm.

Discussions

As far as the equilibrium between free detergent ions and micellar ions is established, the partial molal volume change, ΔV, caused by the micellar formation is expressed by the following equations[1)~4)].

$$\Delta V=\left(\frac{\partial \Delta G}{\partial P}\right)_T=-RT\left(\frac{\partial \ln K}{\partial P}\right)_T=RT\left[\frac{\partial\{(2-Z/n)\ln(\text{c.m.c.})\}}{\partial P}\right]_T \qquad (1)$$

where K stands for the equilibrium constant for the micelle formation. The term $(2-Z/n)$ represents the correction factor due to the association of counter ions to the micelle surface: Z stands for the effective charge of one micelle particle composed of n cations. Assuming the term $(2-Z/n)$ in equation (1) is constant at high pressures and over the temperature range so far investigated, the values of ΔV

3) J. N. Phillips, *Trans. Faraday Soc.*, 51, 561 (1955)
4) S. D. Hamann, *J. Phys. Chem.*, 66, 1359 (1962)

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at atmospheric pressure can be calculated from Fig. 3 by using equation (1). The value of $(2-Z/n)$ is assumed as 1.8 as the mean value for the alkyl dodecyl detergents after the results obtained by the light scattering experiment by Phillips[3] at atmospheric pressure. Table 1 shows the observed values

Table 1 Thermodynamic quantities for the micelle formation of DBAC at 1 atm

Temp. (°C)	c.m.c. (molal)	ΔV(cc mole^{-1})	ΔH(kcal mole^{-1})	ΔS(cal mole^{-1} deg^{-1})
25	0.078	+4.5	−1.28	+4.46
35	0.0815	+0.56	−1.28	+4.51
45	0.084	−2.3	−1.28	+4.57

of ΔV for DBAC at atmospheric pressure at 25, 35 and 45°C. With the increase of temperature, ΔV decreases gradually and changes sign from plus to minus.

Moreover, the partial molal enthalpy change, ΔH, caused by the micelle formation is determined from the effect of temperature on c.m.c. As shown in Fig. 4, there is an approximately linear relationship between $-\log$(c.m.c.) and $1/T$. Therefore, the value of ΔH is constant over the temperature range 25 to 45°C. The observed value of ΔH, −1.3 kcal/mole, is approximately equal to the mean value, −1.0 kcal/mole, obtained for a number of ionic detergents of the dodecyl paraffin chain at about 25 to 35°C[3)5)6)].

Besides, the partial molal entropy change, ΔS, caused by the micelle formation is calculated using ΔH and ΔG at 25°C. The observed positive value of ΔS, about +13 cal/mole·deg, is generally in accordance with the values obtained for other detergents: for example, the value for sodium dodecyl sulfonate is +22 cal/mole·deg at 25°C[3)].

In order to explain the experimental results according to the thermodynamic quantities, it must be kept in mind that the detergent ion has the dual character. In other words, the detergent molecule has the both ionic polar end group and the non-polar hydrocarbon chain.

Considering the value of ΔV, it seems plausible to regard that there is no significant contribution of the polar end group, because the spatial size of the polar end group is insensitive to the value of ΔV[1)]. Accordingly, the value of ΔV could be determined mainly by the nature of the non-polar paraffin chain. The small positive value of ΔV at 25°C would be attributed to the existence of ice-like structure of water[7)]. When free detergent ions are transferred to the micellar component, the ice-like structured water, surrounding the hydrocarbon chain is almost released and thus causes the increase in partial molal volume. The decrease of the value of ΔV with the rise of temperature also supports the above mentioned explanation.

The negative value of ΔV at 45°C could be ascribed to the decrease of electrostatic work needed for the aggregation of the hydrocarbon parts overcoming the repulsion of its polar end groups: the dielectric constant of water increases steadily with temperature. Consequently, the micellar state is

5) B. D. Flockhart, *J. Colloid Science*, **16**, 484 (1961)
6) P. Mukerjee and A. Ray, *J. Phys. Chem.* **70**, 2150 (1966)
7) G. Némethy and H. A. Scheraga, *J. Chem. Phys.* **36**, 3382, 3401 (1962)

denser than the free single ion state.

As for as the small negative value of ΔH over the temperature range 25 to 45°C, it is understood by regarding the micelle formation process as the analogous process to liquefy the gaseous hydrocarbon. According to the extrapolation of the theoretical calculation by Némethy and Scheraga[7], the value of ΔH for the dissolution of liquid *n*-dodecane to pure water would show a small positive value at 25°C: namely, the reverse process needs a small negative value. The increase of the value of ΔH to the positive direction with the rise of temperature over the wide temperature range shown by other workers could be ascribed to the counter-balance due to the decrease of the ice-like structure of water.

For the explanation of the positive value of ΔS over the temperature range investigated, it seems reasonable to take account of both the non-polar hydrocarbon part and the ionic end group. In the temperature range where ice-like structures exist, the hydrocarbon part is released from the restriction when it is transferred to the micellar state in which the hydrocarbon could behave almostly as a pure liquid. On the contrary, at temperatures in which the ice-like structure of water disappears almostly, the decrease of hydration of the polar end group at the micelle surface compared with the single ion state would contributes mainly to the positive valuc of ΔS.

By using the above mentioned thermodynamic considerations, the variation of c.m.c. with high pressure shown in Fig. 3 could be explained as follows; assuming the validity of equation (1) at high pressures, the value of ΔV for DBAC is always negative and about -3 or -4 cc/mole at above 2,000 atm over the temperature range 25 to 45°C. In this pressure and temperature region, it seems that there is no considerable amount of ice-like structure of water around hydrocarbon chain. Therefore with increasing pressure and hence with increasing dielectric constant of water, the electrical work needed for the aggregation of polar functional group of DBAC diminishes gradually: the c.m.c. is depressed monotonously with increasing pressure.

On the contrary, the peculiar behavior of c.m.c. *vs.* pressure curve at 25°C up to about 2,000 atm could be ascribed principally to the "abnormal" structure of water in this pressure and temperature region. Considering the same kind of experiments at 35 and 45°C, it seems likely that this peculiar phenomenon positively supports the existence of ice-like structure of water. The increase of pressure and temperature both favor the destruction of ice-like structure formed around the hydrocarbon chain of cation in the single ion state and thus cause the decrease of the value of ΔV.

In order to elucidate the detailed explanation for the behavior of micelle under high pressure, it is desirable to find a new experimental device to detect the variation of n and Z in equation (1). Moreover, the more plausible theory would be needed for the further work.

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Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan